Dihydrogen Binding in Hydrogenase and Nitrogenase

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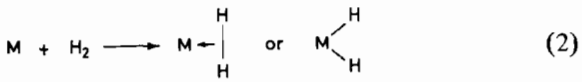
(Received March 13, 1986)

Nickel has been found recently [1] in a number of bacterial hydrogenases which carry out reaction (1).

$$H_2 \rightleftharpoons 2H^+ + 2e^- \quad (1)$$

There is some evidence that nickel may be the binding site for H_2 [2] and the oxidized form of the enzyme shows EPR [1–2] and UV [3] evidence for the presence of Ni(III). Nitrogen and sulfur coordination to nickel from amino acid side chains are considered likely [3, 4], but the details are unclear. H/D exchange between water and H_2 is catalysed by the enzyme [5].

Recent developments in the coordination chemistry of H_2 have led to the recognition of molecular hydrogen complexes of type **1** as distinct from the much more usual binding of H_2 by oxidative addition to give a classical dihydride **2** (eqn. (2)).

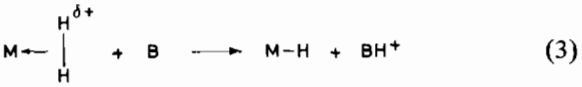


(2)

1 **2**

The first example of a complex of type **1**, $W(H_2)(CO)_3(PCy_3)_2$ (Cy = cyclohexyl), was discovered by Kubas *et al.* [6] and unambiguously confirmed by neutron diffraction. More recently, a considerable number of such species have been detected either by IR [7], X-ray diffraction [8] or relaxation time measurements in the ^1H NMR [9].

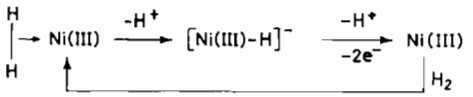
A significant observation is that these complexes can undergo rapid deprotonation by base and, like the enzyme, show isotopic exchange with water [9, 10]. The reason seems to be that the binding is largely H_2 to metal σ-donor in character, leaving



(3)

the H_2 with a partial positive charge [10]. The binding of molecular H_2 does not oxidize the metal as can oxidative addition and so is a particularly appropriate form of binding for high oxidation state metals, such as Ni(III).

The enzyme may therefore operate by binding H_2 and deprotonation as shown in eqn. (4). The



(4)

exact order of proton and electron loss is difficult to assess at present.

There is a second natural system in which the occurrence of dihydrogen complexes needs to be considered. Nitogenase [11] reduces N_2 to NH_3 in various bacteria and blue–green algae. Molybdenum in a sulfur ligand environment is believed to constitute the N_2 binding site [11b]. Not only does the enzyme have hydrogenase activity [11c] in the sense that water is reduced to H_2 in the absence of N_2, but H_2 is also a competitive inhibitor for N_2 reduction. One of the interesting features of some of the compounds recently shown to be dihydrogen complexes is that the analogous N_2 complexes can be formed by direct reaction with N_2, e.g., $FeH_2(L)(PEtPh_2)$ [12] and $W(L)(CO)_3(PCy_3)_2$ [6, 13] (L = H_2 or N_2). The case of $MoH_4(PMePh_2)$ and $Mo(N_2)_2(PMePh_2)_2$ is particularly interesting. Here, the hydride has a classical structure with terminal M–H bonds only [14], and it is formed irreversibly from the N_2 complex. Photolysis does cause H_2 loss from the hydride and the N_2 complex is formed under these conditions [15]. From the limited data available, it appears that only nonclassical molecular hydrogen complexes can be rapidly displaced by N_2 to give the corresponding N_2 complex. This suggests that in nitrogenase too, H_2 may bind in this nonclassical form, rather than as a classical hydride.

Acknowledgements

We thank A.R.O. for support, and Prof. G. Brudvig for discussions.

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